LIGHT ABSORPTION IN NO_3 ION IN STATE OF SOLUTION

(Part III.—Effect of Cation)

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ABSTRACT. 200 $m\mu$ band, which is an allowed $\pi \rightarrow \pi^*$ transition, has been studied in five monovalent nitrates. The blue shift of the band has been found to be proportional to the inverse of the cationic radius.

INTRODUCTION

In the preceding part (Part II) of the present series of papers, a systematic study of the characteristics and assignment of the 200mμ band of nitrate ion has been reported (Mookherji and Tandon, 1965).

Absorption bands are observed to suffer a shift towards shorter wavelength due to the effect of environment known as blue shift. In the state of solution the factors which presumably affect the position of the electronic bands are ion-ion and ion-solvent interactions. The former has not been studied in the case of 200mμ band of the nitrate ion while the latter has been studied in some details (McConnell, 1952, Strickler, 1961, Strickler and Kasha, 1961) and will be discussed in the next paper of the series.

In dilute solutions ion-ion interactions are expected to be very weak and are usually masked by the ion-solvent effect. Ion-ion interactions are of two types, anion-cation and anion-anion. The later interactions are so weak that they can not be recorded. So there is a possibility of studying only the former by investigating the spectral shifts, keeping all other parameters constant and varying the cation. The importance of this lies in the expectation that it may become a tool for making direct measurements of intermolecular interactions.

The present communication reports a systematic study of the effect of cation on the energy of the 200mμ band, which has been assigned to D_{3h} symmetry allowed $\pi \rightarrow \pi^*$ transition of the nitrate ion (Mookherji and Tandon, 1962, 1965) in state of aqueous solution. The results have been discussed in the light of the work of Mott and Gurney, (1948) , Meyerstein and Treinin, (1961) and Smith and Boston (1961).

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EXPERIMENTAL RESULTS

The results of measurements of absorption with UVISPEK spectrophotometer reported earlier (Mookherji and Tandon, 1965) have been used. Energy in electron volts of these peaks- (A B, C, D and E of 200mμ) against inverse of the radius of five monovalent cations, —lithium, sodium, potassium, silver and ammonium, have been given in Fig. 1.

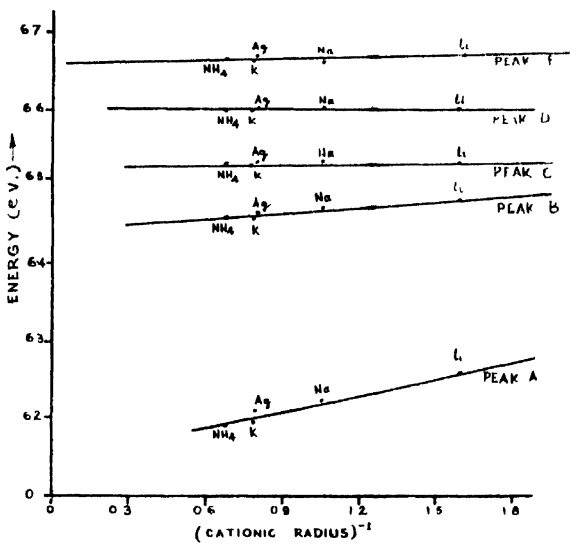

Fig. 1. Variation of energy of peaks A. B. C, D and E of 200$m\mu$ band of nitrate ion with (Cationic radius)$^{-1}$.

DISCUSSION

A study of Fig. 1 reveals a blue shift with decrease of cation radius for the nitrates studied. To explain such band shifts due to environment several theories have been proposed (Griffiths and Symons, 1960a) in connection with the electron transfer spectra. In an aqueous solution there is also possibility of ion-pairs formation. An internal transition in an anion, brings about only a limited expansion of the electronic orbital, and hence will be probably affected only by the external polarizing effect of the cations (Kortum, 1944; Griffiths and Symons, 1960b) suggesting that the cation would affect the spectrum of anion only at contact approach. But in the present case of nitrate ion, it is possible for the cationic effect to be conveyed (Meyerstein and Treinin, 1961) through the first hydration layer. In dilute aqueous solutions solvated cations which have the nitrate ions as nearest neighbours may be attached quite firmly to the cation. This is the case of local hydrolysis (Diamond, 1958), and is an extreme case of polarization. The polarized water must be more H-bonded to nitrate ion and thus will act as a more polar solvent than ordinary water. The magnitude of the ionic effects

will depend on the charge on the cation, distance and mode of approach to the nitrate ion. Thus the cations having only one water molecule separating them from nitrate ion are expected to have an effect decreasing with increasing cationic radii. This is what has been observed. But this mechanism of band shift is analogous to that of electron transfer spectra. It has already been proved (Mc Ewen, 1961; Strickler and Kasha, 1961; Mookherji and Tandon, 1962, 1965) that the spectrum of the nitrate ion is not due to electron transfer, but due to an allowed $\pi \rightarrow \pi^*$ transition, which shifts the electronic charge density from the region round oxygen atoms to the region around nitrogen atom. Consequently the blue shift may be explained as follows :

In solution (Mott and Gurney, 1948) like crystal and melt (Smith and Boston, 1961) there exist two types of forces, Coulomb and Overlap forces. The Coulomb forces of the other ions give rise to the external electrostatic potential, V, arising from pairwise electrostatic interaction between ions. For solutions containing N ions, we have then

$$V(rONO_3) = \sum_{i=1}^{N-1} \frac{e}{D} \int \frac{\rho_i(r_i)}{rNO_3 - r_i} \, dV_i \qquad \ldots \quad (1)$$

Where r_{NO_3} is the vector position of the volume element (dV_{NO_3}) in the nitrate ion that becomes excited, r_i is the vector position of a volume element dV_i in the i-th ion, $\rho_i(r_i)$ is the charge density function of the i-th ion, e is the electronic charge and D is effective dielectric constant. The term $r_{NO_3} - r_i$ is the scalar distance between dV_{NO_3} and dV_i.

The external electrostatic potential V is positive because nitrate ion is negative. The dipole and higher terms in V are produced primarily by neighbouring ions. Therefore it is useful to divide the ions into two groups : those ions which lie nearest to a given nitrate ion and those ions which are more remote. The nearest neighbours are cations and are assumed to have rare-gas-electronic configurations, with small polarization terms ignored. These cations can be represented as point charges and the following change made in equation (1) :

$$V(r_{NO_3}) = \sum_{i=1}^{C} \frac{e}{D} \int \frac{Z_i}{(r_{NO_3})_i} \, dV_{NO_3} + V_{other} \qquad \ldots \quad (2)$$

Where Z_i is the net charge or electrostatic valence of the i-th cation, (r_{NO_3}) is the scalar distance from the centre of the i-th cation to the volume element dV_{NO_3} of the nitrate ion, the summation is over the C-cations of the nearest neighbour shell, and V is the term similar to equation (1) but is summed from $(C+1)$ through $(N-1)$. The dipole and higher terms in equation (2) are of greatest magnitude near the neighbour cations where they increase as the cationic Z/r_0 increase.

The potential V as discussed above contributes to the transition energy in a way approximately described by (Smith *el al*, 1961).

$$(h\nu)_{max} = (h\nu)_0 + e\int (|\psi_{ex}|^2 - |\psi_{gr}|^2) V dV \quad \ldots \quad (3)$$

where $(h\nu)_0$ represents the transition energy for a nitrate ion separated to infinity including the effect of repulsive overlap forces and the integral represents the change in interaction energy between V and the electronic charge cloud of the nitrate ion in going from the ground to the excited states $|\psi_{gr}|^2$ and $|\psi_{ex}|^2$ are the electronic density functions of the ground and the excited states respectively, and the integral is over the volume of the nitrate ion since dipole and higher terms in equation (2) are of great magnitude near the neighbouring cations, where they increase as the cationic Z/r_0 increase. Consequently the interaction integral in equation (3) changes when Z/r_0 changes. This explains the observed dependence of energy of the 200mμ band on $1/r_0$.

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